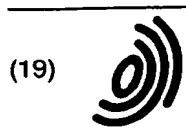


03



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 026 222 A2**

(12) **EUROPEAN PATENT APPLICATION**

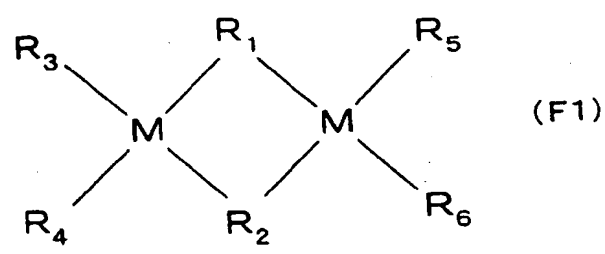
(43) Date of publication: 09.08.2000 Bulletin 2000/32  
(51) Int. Cl.<sup>7</sup>: C09K 11/06, H05B 33/14  
(21) Application number: 00102058.5  
(22) Date of filing: 02.02.2000

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI  
(30) Priority: 04.02.1999 JP 2746899  
22.06.1999 JP 17498799  
29.07.1999 JP 21471299  
(71) Applicant:  
Matsushita Electric Industrial Co., Ltd.  
Kadoma-shi, Osaka-fu, 571-8501 (JP)

(72) Inventors:  
• Matsuo, Mikiko  
Nara-shi, Nara 631-0013 (JP)  
• Kishimoto, Yoshio  
Hirakata-shi, Osaka 573-0083 (JP)  
• Satou, Tetsuya  
Kadoma-shi, Osaka 573-0030 (JP)  
• Hisada, Hitoshi  
Toyonaka-shi, Osaka 565-0085 (JP)  
• Sugiura, Hisanori  
Hirakata-shi, Osaka 573-0049 (JP)  
(74) Representative:  
Blumbach, Kramer & Partner GbR  
Radeckestrasse 43  
81245 München (DE)

(54) **Organic material for electroluminescent device and electroluminescent device using the same**

(57) A new organic material for an electroluminescent device suitable for an electroluminescent device and an electroluminescent device using the same. The organic material uses a complex compound expressed by the following formula (F1):



wherein R1 and R2, which can be same or different, respectively denote one selected from the group consisting of halogen, alkyl having 1 to 3 carbon atoms, and a bridging ligand having a nitrogen-containing aromatic ring containing at least two nitrogen atoms, and when R1 or R2 is a bridging ligand having a nitrogen-containing aromatic ring, nitrogen in the nitrogen-containing aromatic ring is a coordinating atom; R3, R4, R5 and R6, which can be same or different, respectively denote one member selected from the group consisting of hydrogen, alkyl, aryl, an aryl derivative, a nitrogen-containing aromatic ring and a derivative of a nitrogen-containing aromatic ring; and M is a central metal.

EP 1 026 222 A2

## Description

[0001] The present invention relates to an organic material for an electroluminescent device and an electroluminescent (EL) device using the same.

[0002] An electroluminescence panel is characterized by high visibility, excellent display performance and a high-speed response. Recently, an organic electroluminescent device (hereinafter referred to also as EL device) using organic compounds is reported (see, for example, relevant document in "Applied Physics Letters," Vol. 51, p913, 1987). This document describes an organic EL device having a structure in which a hole transport layer and an organic light emitting layer are laminated.

[0003] The structure of conventional organic EL devices is explained with reference to Figs. 11 to 14.

[0004] An organic EL device 1 of Fig. 11 includes a glass substrate 2, an anode 3 laminated on the glass substrate 2, an organic light emitting layer 4 and a cathode 5. The anode 3 is a transparent electrode.

[0005] An organic EL device 1a of Fig. 12 is called an SH-A type device. The organic EL device 1a includes a glass substrate 2, an anode 3 laminated on the glass substrate 2, a hole transport layer 6, an organic light emitting layer 4 and a cathode 5. The above-mentioned report by Tang et al. relates to the organic EL device 1a, which uses a tris (8-quinolinolato) aluminum (hereinafter, referred to also as Alq) for the organic light emitting layer 4. This Alq is an excellent light emitting material having both high luminous efficiency and high electron transporting property. Another type of the organic EL device 1a is a device in which Alq, which forms the organic light emitting layer 4, is doped with a fluorescent dye such as a coumarin derivative or DCM1, etc. (see Journal of Applied Physics, Vol. 65, p3610, 1989). According to the organic EL device 1a, the luminescent colors can be varied and the luminous efficiency can also be improved by selecting appropriate dyes.

[0006] An organic EL device 1b of Fig. 13 is called an SH-B type device. The organic EL device 1b includes a glass substrate 2, an anode 3 laminated on the glass substrate 2, an organic light emitting layer 4, an electron transport layer 7 and a cathode 5. For the electron transport layer 7, an oxadiazole derivative, typically 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (hereinafter, referred to also as PBD), is often used. However, the oxadiazole derivative such as PBD etc. tends to be crystallized and is not suitable for practical use.

[0007] An organic EL device 1c of Fig. 14 is called a DH type device. The organic EL device 1c includes a glass substrate 2, an anode 3 laminated on the glass substrate 2, a hole transport layer 6, an organic light emitting layer 4, an electron transport layer 7 and a cathode 5.

[0008] At present, the SH-A type devices of Fig. 12 or the DH type devices of Fig. 14 are mainly studied and developed. As to the electron transport layer, the hole transport layer and the light emitting layer, new materials suitable for each layer's function have been developed and studied. In particular, as a hole transporting organic molecule used for the hole transport layer, a large number of materials derived from triphenylamine have been developed. Furthermore, for a fluorescent organic molecule used for the light emitting layer, a fluorescent pigment, a laser dye, etc. can be used.

[0009] Furthermore, the cathode 5 is stable and can easily inject electrons when the cathode 5 is made of an alloy of an alkali metal or an alkaline-earth metal having a low work function and a stable metal such as aluminum or silver, etc. According to one report, for example, by controlling a Li concentration contained in the alloy to be such a slight amount as 0.01 wt.% or more and 0.1 wt.% or less, an EL device can exhibit a high luminous efficiency and high stability (see, for example, Publication of Japanese Patent Application No. Hei 5-121172 A). Furthermore, according to another report, a cathode in which a thin film made of a metal having a low work function is formed as an electron injection electrode on the side of an organic compound layer, and a thin film made of a stable metal is formed thereon as a protective electrode. With such a cathode structure, since it is not necessary to control the concentration of an alkaline metal such as Li, etc. having a high reactivity with water, a cathode that easily can be manufactured can be obtained.

[0010] Furthermore, an organic EL device in which an electron injection layer is placed on the cathode at the side of the organic layer is also reported. For example, the organic EL device using an alkaline metal compound for the electron injection layer and optimizing the thickness of this electron injection layer is disclosed (see Publication of Japanese Patent Application No. Hei 9-17574A). Furthermore, the relationship between the thickness of these electron injection layers and a dark spot is reported in detail (T. Wakimoto, Y. Fukuda, K. Nagayama, A. Yokoi, H. Nakada and M. Tsuchida, IEEE Transactions on Electron Devices, Vol. 44, No. 8, p1245, 1997).

[0011] As mentioned above, in the organic EL device, the electron injection layer has been studied as an important factor for determining the luminous efficiency and lifetime.

[0012] However, conventional organic EL devices do not have satisfactory luminous efficiency, selectivity of emission wavelength and lifetime.

[0013] In particular, when the light emitting layer is formed by a doping method, it is difficult to control the concentration of a dopant. Furthermore, guest materials for emitting red light have a wide range of  $\pi$  electron system, so that they tend to be interacted with each other and are easily subjected to concentration quenching.

[0014] It is therefore an object of the present invention to provide an organic material suitable for an electroluminescent device and an electroluminescent device using the same.

ring. With such a structure, an EL device emitting various colors of light can be obtained.

[0026] It is preferable in the above-mentioned EL device that the organic compound layer further includes diphenylanthracene or a diphenylanthracene derivative. With such a structure, an EL device emitting various colors of light can be obtained.

5 [0027] It is preferable in the above-mentioned EL device that the organic compound layer further includes a compound having a ring structure that is the same as the ring structure of at least one member selected from the group consisting of pyrrole, imidazole, pyrazole, triazole, pyridine, pyridazine, pyrazine, pyrimidine, triazine, tetrazine, oxazole and oxadiazole. With such a structure, an EL device emitting various colors of light can be obtained.

[0028] It is preferable in the above-mentioned EL device that the peak of the photoluminescence of the compound is 580 nm or more and 680 nm or less. With such a structure, an EL device emitting orange to red light can be obtained.

10 [0029] It is preferable in the above-mentioned EL device that the organic compound layer further comprises an aromatic-substituted amine or a derivative thereof. With such a structure, an EL device having high luminance and emitting a blue light that has high color purity can be obtained.

[0030] It is preferable in the above-mentioned EL device that the organic compound layer further comprises an organic compound forming an exciplex with the organic material. With such a structure, an EL device having a high luminance and emitting various luminescent colors can be obtained.

[0031] It is preferable in the above-mentioned EL device that the organic compound is pyrene or a pyrene derivative. With such a structure, an EL device having a particularly high luminance can be obtained.

20 [0032] It is preferable that the above-mentioned EL device further includes a second organic compound layer placed between the cathode and the light emitting layer and that the second organic compound layer includes the above-mentioned first organic material for an EL device. With such a structure, an EL device, which is not effected by concentration quenching and which emits various colors of light, can be obtained.

[0033] It is preferable that the above-mentioned EL device further includes a hole transport layer between the anode and the light emitting layer. With such a structure, an EL device having a particularly high luminous efficiency can be obtained.

25 [0034] It is preferable in the above-mentioned EL device that the organic compound layer is an electron transport layer or an electron injection layer. With such a structure, an EL device having a particularly high luminous efficiency can be obtained.

[0035] It is preferable that the above-mentioned EL device further includes a light emitting layer between the organic compound layer and the anode.

30 [0036] It is preferable that the above-mentioned EL device further includes a hole transport layer between the light emitting layer and the anode. With such a structure, an EL device having a particularly high luminous efficiency can be obtained.

[0037] It is preferable in the above-mentioned EL device that the organic compound layer is an electron injection layer and the thickness of the organic compound layer is 0.2 nm to 2 nm. With such a structure, the organic compound layer works as an electron injection layer and an EL device having a particularly high luminous efficiency can be obtained.

40 [0038] It is preferable in the above-mentioned EL device that the concentration of the organic material contained in the organic compound layer increases toward the side of the cathode. With such a structure, an EL device having a particularly high luminous efficiency can be obtained.

[0039] It is preferable in the above-mentioned EL device that the cathode is made of a metal having a work function of 4.0 eV or more. With such a structure, the cathode is hardly deteriorated, so that an EL device having a long lifetime and high reliability can be obtained.

45 [0040] It is preferable in the above-mentioned EL device that the cathode is made of at least one metal selected from the group consisting of Al, Ag, In and Bi.

Fig. 1 is a sectional view showing an EL device of one example according to the present invention.

Fig. 2 is a sectional view showing an EL device of another example according to the present invention.

Fig. 3 is a sectional view showing an EL device of a further example according to the present invention.

50 Fig. 4 is a sectional view showing an EL device of a further example according to the present invention.

Fig. 5 is a sectional view showing an EL device of a further example according to the present invention.

Fig. 6 is a sectional view showing an EL device of a further example according to the present invention.

Fig. 7 is a sectional view showing an EL device of a further example according to the present invention.

Fig. 8 is a sectional view showing an EL device of a further example according to the present invention.

55 Fig. 9 is a sectional view showing an EL device of a further example according to the present invention.

Fig. 10 is a sectional view showing an EL device of a further example according to the present invention.

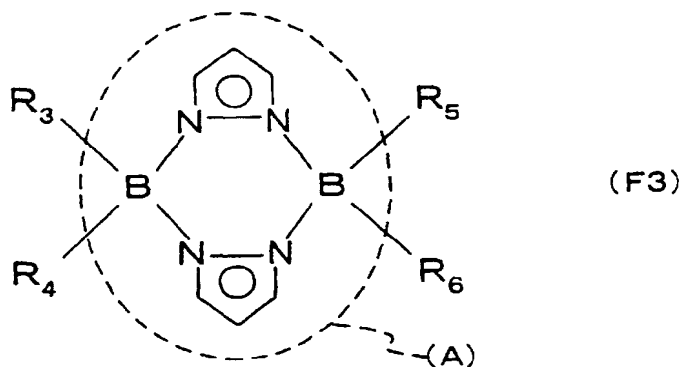
Fig. 11 is a sectional view showing an EL device of an example of the prior art.

Fig. 12 is a sectional view showing an EL device of an example of the prior art.

cifically, for example, a methyl group, an ethyl group, a phenyl group, a tolyl group, a naphthyl group, a biphenyl group, an anthranil group, a 9-phenylanthranil group or a pyrenyl group, or the like, can be used. Among the nitrogen-containing aromatic rings that can be used for R3 to R6, examples containing one nitrogen atom include pyrrole, pyridine, oxazole, and the like; examples containing two or more nitrogen atoms include a nitrogen-containing aromatic ring having a ring structure that is the same as the ring structure of imidazole, pyrazole, pyridazine, pyrazine, pyrimidine, oxadiazole, triazole, triazine, tetrazine, tetrazole or phenanthroline. For example, 2,9-dimethylphenanthroline can be used. Furthermore, hetero-multiply condensed ring in which an aromatic ring is condensed to a nitrogen containing aromatic ring having 5 or less carbon atoms, for example, carbazole or benzimidazole, is also included in the nitrogen-containing aromatic ring having 5 or less carbon atoms of the present invention. Such a ring has the same effect as the above-mentioned nitrogen-containing aromatic ring.

**[0051]** The aryl derivative and the nitrogen containing aromatic ring derivative shown by R3 to R6 respectively denote an aryl derivative and nitrogen-containing aromatic ring derivative further including a substituent of halogen, a phenyl group, and the like, or denote a condensed ring, each of which can maintain the aromatic property of the above-mentioned aryl or nitrogen-containing aromatic ring.

**[0052]** It is preferable that the complex compound (F1) has a pyrazabole structure expressed by (A) in the following formula (F3).



**[0053]** Examples of the complex compound (F1) having a pyrazabole structure include the following compounds A-1 to A-6.

- A-1: pyrazabole
- A-2: 1, 3, 5, 7-tetramethyl pyrazabole
- A-3: 4, 4, 8, 8-tetraethyl pyrazabole
- A-4: 4, 4, 8, 8-tetrakis (1H-pyrazol-1-yl) pyrazabole
- A-5: 4, 4, 8, 8-tetrakis (1H-pyridazin-1-yl) pyrazabole
- A-6: 4, 4, 8, 8-tetrakis (1H-benzimidazol-1-yl) pyrazabole

**[0054]** The above A-1 to A-4 are available from Aldrich ACROS ORGANICS. The A-5 and A-6 can easily be synthesized from pyrazabole.

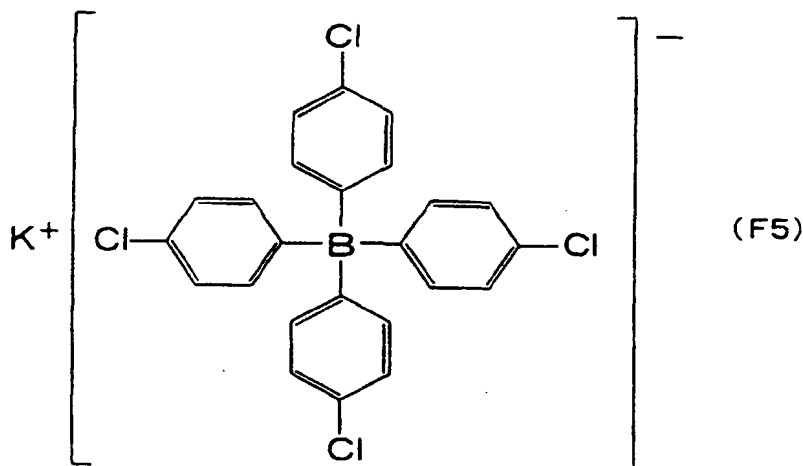
**[0055]** Specifically, A-5 and A-6 can be obtained by refluxing pyridazine or benzimidazole and trimethylamine borane in the ratio of 1:1 in toluene.

**[0056]** As one example, the structure of A-4 is expressed below in the structural formula (F4).

wherein R7 to R9, which can be same or different, respectively denote an electron accepting phenyl group.

**[0064]** The electron accepting phenyl group that can be used for R7 to R9 includes a phenyl group substituted by an electron accepting group such as a halogen, a cyano group, a nitro group, a carbonyl group and the like. The above-mentioned complex compound (F2) has an electron accepting aromatic ring in a ligand forming a stable organic boron complex compound, thus forming an excellent fluorescent light emitting film.

**[0065]** An example of the organic boron complex compound having a ligand that is a phenyl group substituted by halogen, for example, an organic boron complex salt having a tetrakis (halophenyl) borate structure. An example of the organic boron complex salt having a tetrakis (halophenyl) borate structure is potassium tetrakis (4-chlorophenyl) borate expressed by the following formula (F5).



**[0066]** As a halogen element used for tetrakis (halophenyl) borate, fluorine has the highest electron accepting property and is also chemically stable. A specific example includes, for example, magnesium tetrakis(4-fluorophenyl) borate.

**[0067]** Thus, the organic material for an EL device of the second embodiment can provide a high luminance and various luminescent colors.

**[0068]** In the second embodiment, the above-mentioned alkyl group preferably has 1 to 8 carbon atoms. In the second embodiment, the above-mentioned aryl group preferably has 1 to 30 carbon atoms.

**[0069]** In another aspects of this invention, this invention relates to the use of the above-mentioned organic materials for the EL devices.

#### (Third Embodiment)

**[0070]** In the third embodiment, an example of EL devices according to the present invention is explained.

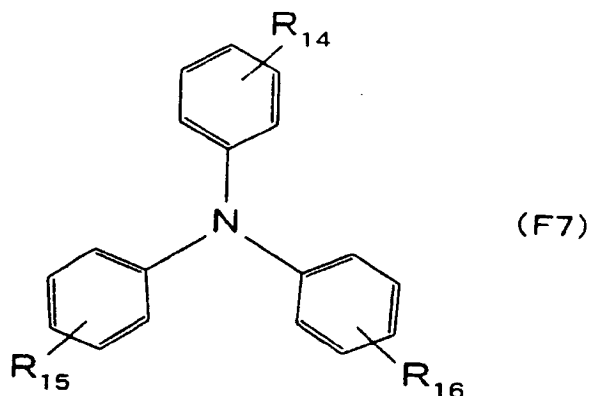
**[0071]** Fig. 1 is a sectional view showing an EL device 10 of the third embodiment. Referring to Fig. 1, the EL device 10 includes a translucent substrate 11, and an anode 12, a light emitting layer 13 and a cathode 14, which are sequentially laminated in that order on the translucent substrate 11. That is, the light emitting layer 13 is placed between the anode 12 and the cathode 14.

**[0072]** For the translucent substrate 11, a material capable of supporting the anode 12 etc. and transmitting light from the light emitting layer 13 can be used. Specifically, for example, a glass such as Corning 1737 etc. or a resin film made of polyester or the like can be used.

**[0073]** The anode 12 is an electrode for injecting holes. For the anode 12, a transparent electrode film such as ITO (Indium Tin Oxide) or SnO<sub>2</sub> and the like can be used. Also, a thin film made of a metal such as Ni, Au, Pt, Pd or the like can be used. The thickness of the anode 12 is determined by taking into account a sheet resistance value and transmittance of visible light. Usually, the thickness is made to be 100 nm or more in order to reduce the sheet resistant value. The anode 12 can be formed by, for example, a sputtering method, an electron-beam evaporation, ion plating, and the like.

**[0074]** The cathode 14 is an electrode for injecting electrons. The cathode 14 can be formed, for example, by laminating a metal film made of an alkali metal or an alkaline earth metal and a stable metal film made of aluminum or silver,

wherein R10 and R11, which can be same or different, respectively denote one selected from the group consisting of hydrogen, a methyl group, a methoxy group and Cl; and R12 and R13, which can be same or different, respectively denote one selected from the group consisting of hydrogen, an alkyl group, an alkoxy group, a phenyl group and a phenyl group substituted by an alkyl group or an alkoxy group.



wherein at least one of R13, R14 and R15 is styryl, phenylstyryl, naphthylstyryl, or a derivative thereof substituted by an alkyl group, an amino group or a phenyl group; and R13, R14 and R15 other than the above are respectively made of an alkyl group, an amino group, phenyl group, alkyl-substituted benzene, or amino-substituted benzene.

**[0084]** Specifically; for the compound (F6), N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-binaphthyl-1,1'-biphenyl-4,4'-diamine, N,N'-bis(4'-diphenylamino-4-biphenyl)-N,N'-diphenylbenzidine, and the like, can be used. Furthermore, for the compound (F7), it is possible to use 4-N, N'-diphenylamino- $\alpha$ -phenylstilbene, 4-N, N'-bis(p-methylphenyl)amino- $\alpha$ -phenylstilbene, 4-N, N'-diphenylamino- $\alpha$ -naphthylstilbene, 4, 4'-bis( $\alpha$ -phenylstyryl)triphenylamine, 4, 4',4''-tri( $\alpha$ -phenylstyryl)triphenylamine, 4, 4'-bis(3-methylphenylstyryl)triphenylamine, 4, 4'-bis(2, 4-dimethylphenylstyryl)triphenylamine, 4, 4'-bis( $\alpha$ -biphenylstyryl)triphenylamine, and the like. These compounds emit blue light having a peak between 430nm and 490nm in a solution or in a state of thin film. It is preferable that the light emitting layer 13 includes the complex compound (F1) and aromatic-substituted amine (or a derivative thereof) and the amount of the aromatic-substituted amine (or a derivative thereof) is in the range from 1 wt% to 50wt%.

**[0085]** Moreover, the above-mentioned EL device 10 is just an example. Therefore, other embodiments may be employed as long as the EL device has the light emitting layer 13. Other examples of such EL devices are shown in Figs. 2 to 8.

**[0086]** The EL device 10a of Fig.2 further includes an electron transport layer 15 between the light emitting layer 13 and the cathode 14, in addition to the structure of the EL device 10. The EL device 10b shown in Fig. 3 further includes an electron injection layer 16 between the light emitting layer 13 and the cathode 14, in addition to the structure of the EL device 10. The EL device 10c shown in Fig. 4 further includes an electron transport layer 15 and an electron injection layer 16 between the light emitting layer 13 and the cathode 14, in addition to the structure of the EL device 10. The electron transport layer 15 and the electron injection layer 16 are sequentially laminated on the light emitting layer 13 in that order from the side of the light emitting layer 13. Moreover, the EL devices 10 and 10a to 10c may further include a hole transport layer 17 between the anode 12 and the light emitting layer 13. The embodiments in which the EL devices 10, 10a, 10b, and 10c further include a hole transport layer 17 are shown in Fig. 5 (an EL device 10d), Fig. 6 (an EL device 10e), Fig. 7 (an EL device 10f) and Fig. 8 (an EL device 10g), respectively.

**[0087]** Since the translucent substrate 11, an anode 12, a light emitting layer 13 and a cathode 14 in the EL devices 10a to 10g are the same as those of the EL device 10, the explanation thereof will be herein omitted.

**[0088]** For the electron transport layer 15, for example, tris(8-quinolinolato) aluminum (hereinafter, referred to also as Alq), tris(4-methyl-8-quinolinolato) aluminum or 3-(2'-benzothiazolyl)-7-diethylaminocoumarin, or the like, can be used. In other words, for the electron transport layer 15, an organic compound having a higher energy level of LUMO (Lowest Unoccupied Molecular Orbital) than the compound constituting the light emitting layer 13, or an inorganic compound having a smaller electron affinity than the compound constituting the light emitting layer 13 can be used. The thickness of the electron transport layer 15 is preferably in the range from 10 nm to 1000 nm.

**[0089]** For the electron injection layer 16, for example, an inorganic compound such as LiF, Li<sub>2</sub>O or CaO, or an organic compound such as 8-quinolinolato lithium, tetrapyrroldiporphine cobalt, or the like can be used. In other words, for the electron injection layer 16, an inorganic compound having a smaller electron affinity than the compound consti-

emitting layer 91 are different from usual dopants and are not required to have the luminescent peak that is intended. Therefore, the overlapping of spectra necessary for energy transfer are not required and so there is no interaction of materials or concentration quenching due to a wide range of  $\pi$  electron system of dye. For example, Publication of Japanese Patent Application No. Hei 10-159076 A discloses the EL device provided with a blocking layer between the electron transport layer and the hole transport layer in order to prevent the shift from the original luminescent color of the dopant. However, the EL device 90 does not need such a blocking layer. The EL device 90 forms the exciplex in the light emitting layer and emits light from the exciplex. That is, even if an individual organic molecule has a small fluorescent intensity, by forming the exciplex with these molecules, it is possible to produce a new electron state and to achieve a strong luminescence. Furthermore, the exciplex is formed not only in the case where entire molecules are interacted with each other but also in the case where an electron acceptor part or an electron donor part in each molecule are interacted with each other. Therefore, by finding the combination thereof, an EL device with high luminescence and various colors can be obtained.

#### (Fifth Embodiment)

[0103] In the fifth embodiment, another example of an EL device according to the present invention is explained.

[0104] Fig. 10 is a sectional view showing an EL device 100 of the fifth embodiment. The EL device 100 includes a translucent substrate 11, an anode 12, a light emitting layer 101, an organic compound layer 102 and a cathode 103, which are sequentially laminated on the translucent substrate 11 in that order.

[0105] For the light emitting layer 101, an organic compound having a narrower band-gap than that forming the organic compound layer 102 can be used. Specifically, for example, Alq or a derivative thereof can be used. Moreover, for Alq or a derivative thereof which is doped with a dye such as coumarin 6, a dicyanomethylene derivative (commercial name: DCM, produced by LAMBDA PHYSIK) or phenoxazone 9 may be used for the light emitting layer 101. Furthermore, for the light emitting layer 101, triphenylamine doped with rubrene may be used. Furthermore, the light emitting layer 101 may be formed by a material having a hole transport property and a hole block layer of bathocuproin etc. may be formed at the interface between the light emitting layer 101 and an electron transport layer. Moreover, since the complex compound (F1) emits violet light by itself, by using an appropriate material for the light emitting layer 101, it is possible to obtain an EL device that emits light having a longer wavelength than the violet light.

[0106] The organic compound layer 102 includes the complex compound (F1) explained in the first embodiment. The complex compound (F1) included in the organic compound layer 102 preferably has a pyrazabole structure. Specifically, A-1 to A-6 of the first embodiment can be used. Above all, an organic compound layer 102 is preferably includes A-4.

[0107] When the thickness of the organic compound layer 102 is large, the organic compound layer 102 works as an electron transport layer. Furthermore, when the thickness of the organic compound layer 102 is thin, the organic compound layer 102 works as the electron transport layer. When the organic compound layer 102 is the electron transport layer, the thickness of the organic compound layer 102 is preferably in the range from 10nm to 1000nm. When the organic compound layer 102 is the electron injection layer, the thickness of the organic compound layer 102 is preferably in the range from 0.1 nm to 5 nm, more preferably in the range from 0.2nm to 2nm.

[0108] It is preferable that the organic compound layer 102 includes the complex compound (F1) in the amount of 0.1 wt% to 99.9 wt%. In particular, it is preferable that the organic compound layer 102 includes the complex compound (F1) in the amount of 50 wt% to 99.9 wt% in about one-third part of the organic compound layer 102 at the side of the cathode. The organic compound layer 102 may include the complex compound (F1) uniformly over the entire layer. Also, the organic compound layer 102 may include the complex compound (F1) so that the concentration of the complex compound (F1) increases toward the side of the cathode 103.

[0109] For the cathode 103, besides materials usually used for cathodes (the material explained as to the cathode 14 of the third embodiment), a stable metal having a work function of 4.0 eV or more can be used. Examples of such a metal include, for example, Al, Ag, In and Bi. Therefore, it is preferable that the cathode 103 is made of at least one metal selected from the group consisting of Al, Ag, In and Bi. The thickness of the cathode 103 is preferably in the range from 10 nm to 1000 nm.

[0110] Moreover, the EL device 100 is not limited to the configuration shown in Fig. 10. For example, the EL device 100 may include a hole transport layer or a hole injection layer between the anode 12 and the light emitting layer 101. Furthermore, when the organic compound layer 102 is the electron injection layer, the EL device 100 may further include an electron transport layer between the light emitting layer 101 and the organic compound layer 102. Furthermore, when the organic compound layer 102 is the electron transport layer, the EL device 100 may further include an electron injection layer between the organic compound layer 102 and the cathode 103.

[0111] The above-mentioned EL device 100 of the fifth embodiment includes an organic compound layer 102 between a light emitting layer 101 and the cathode 103, and the organic compound layer 102 includes the complex compound (F1) explained in the first embodiment. As explained in the first embodiment, the complex compound (F1) is

When a DC voltage was applied to the EL device of Example 5, red light (peak wavelength: 600nm, half band width at peak: 120nm) was emitted. The luminous efficiency was 1.0 cd/A.

#### Example 6

[0120] In Example 6, an EL device was produced similarly to Example 1 except for a light emitting layer. In the EL device of Example 6, 70 wt% of A-4 and 30 wt% of 2, 4-bis(5,6-diphenyl-1, 2, 4-triazine-3-yl)pyridine were codeposited to form a light emitting layer. When a DC voltage was applied to the EL device of Example 6, red light (peak wavelength: 590nm, half band width at peak: 105nm) was emitted. The luminous efficiency was 2.0cd/A.

#### Example 7

[0121] In Example 7, an EL device was produced similarly to Example 1 except for a light emitting layer. In the EL device of Example 7, 80wt% of A-4 and 20wt% of 4-N, N'-bis(p-methylphenyl)amino- $\alpha$ -phenylstilbene were codeposited to form a light emitting layer. When a DC voltage was applied to the EL device of Example 7, blue light (peak wavelength: 460nm) was obtained. The luminous efficiency was 2.8 cd/A, and the EL device continued to emit light stably.

#### Example 8

[0122] In Example 8, an EL device was produced similarly to Example 1 except for a light emitting layer. In the EL device of Example 8, 80wt% of A-4 and 20wt% of 4, 4'-bis( $\alpha$ -phenylstyryl)triphenylamine were codeposited to form a light emitting layer. When a DC voltage was applied to the EL device of Example 8, blue light (peak wavelength: 460nm) was emitted. The luminous efficiency was 3.4 cd/A and the EL device continued to emit light stably.

#### Example 9

[0123] In Example 9, an EL device was produced similarly to Example 1 except for a light emitting layer. In the EL device of Example 9, 80wt% of A-4 and 20wt% of phenylstyrylpyrene were codeposited to form a light emitting layer. When a DC voltage was applied to the EL device of Example 9, pale blue light (peak wavelength: 480nm) was emitted. The luminous efficiency was 5.2 cd/A, and the EL device continued to emit light stably.

#### Example 10

[0124] In Example 10, first, an ITO film was formed on a glass substrate. Then, on the ITO film, a hole transport layer (thickness: 50nm) made of N,N'-bis(4'-diphenylamino-4-biphenyl)-N,N'-diphenylbenzidine was formed. Thereafter, by depositing Alq, the organic light emitting layer (thickness: 20nm) was formed. Then, by depositing A-4, an organic electron transport layer (thickness: 40nm) was formed. Finally, a cathode made of Al was formed. Thus, the EL device of the present invention was produced. When a DC voltage was applied to the EL device, green light (peak wavelength: 520nm) was emitted from Alq. The luminous efficiency was 4.0 cd/A, and the EL device continued to emit light stably. Moreover, the same results were obtained when A-1 to A-3 were used instead of A-4.

#### Example 11

[0125] In Example 11, first, an ITO film was formed on a glass substrate. Then, on the ITO film, an organic light emitting layer (thickness: 50nm) made of 90 wt% of A-2 and 10 wt% of phenylstyrylpyrene was formed. Then, by depositing A-4, an organic electron transport layer (thickness: 50nm) was formed. Finally, a cathode was formed by laminating a Li film and an Al film. Thus, the EL device of the present invention was produced. When a DC voltage was applied to the EL device, blue-green light (peak wavelength: 470nm) was emitted. The luminous efficiency was 2.0cd/A, and the EL device continued to emit light stably.

#### Example 12

[0126] In Example 12, first, an ITO film was formed on a glass substrate. A dye solution was prepared by dissolving polyvinylcarbazole, 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole and coumarin 6 (laser dye) in a solvent in a weight ratio of 100 : 40 : 0.2, respectively. For the solvent, a mixture in which toluene and THF (tetrahydrofuran) were mixed in the weight ratio of 1:1 was used. Next, the dye solution was spread on the ITO film with a spinner, thus forming an organic light emitting layer (thickness: 100 nm). Next, an organic electron injection layer was formed by depositing A-4 onto the organic light emitting layer. Finally, a cathode (thickness: 100nm) made of Al was formed. In Example 12,



Example 17

[0131] In Example 17, first, an ITO film was formed on a glass substrate. Next, on the ITO film, a hole transport layer (thickness: 50nm) made of N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine was formed. Next, 90wt% of Alq and 10wt% of A-4 were codeposited, thereby forming a light emitting layer (thickness: 50nm). Finally, a cathode (thickness: 100nm) made of Al was formed. When a DC voltage was applied to the thus produced EL device, stable luminescence was obtained. When the DC voltage was 5V, the luminance was about 500 cd/m<sup>2</sup>, and the luminous efficiency was 4.5 cd/A. When a continuous lighting test with constant current was carried out to these EL devices under the condition of the initial luminance of 300cd/m<sup>2</sup>, the half value period of luminance was about 580 hours.

Example 18

[0132] In Example 18, first, an ITO film was formed on a glass substrate. Next, on the ITO film, an organic light emitting layer (thickness: 50nm) was formed by codepositing 98wt% of N,N'-bis(4'-diphenylamino-4-biphenyl)-N,N'-diphenylbenzidine and 2wt% of rubrene. Next, by codepositing 90wt% of tris(4-methyl-8-quinolinolato)aluminum and 10wt% of A-2, an electron transport layer (thickness: 50nm) was formed. Finally, a cathode (thickness: 100nm) made of Al was formed. When a DC voltage was applied to the thus produced EL device, stable luminescence was obtained. When the DC voltage was 4V, the luminance was about 550 cd/m<sup>2</sup> and luminous efficiency was 8.4 cd/A. When a continuous lighting test with constant current was carried out on the EL device under the condition of initial luminance of 300 cd/m<sup>2</sup>, the half value period of the luminance was about 12000 hours.

Example 19

[0133] In Example 19, first, an ITO film was formed on a glass substrate. On the ITO film, a hole transport layer (thickness: 50nm) made of N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine was formed. Next, by codepositing 99.5wt% of Alq and 0.5wt% of Quinacridone, an organic light emitting layer (thickness: 20nm) was formed. Next, by codepositing 90wt% of Alq and 10wt% of A-2, an electron transport layer (thickness: 30nm) was formed. Finally, a cathode (thickness: 100nm) made of Al was formed. When a DC voltage was applied to the thus produced EL device, stable luminescence was obtained. When the DC voltage was 4.5V, the luminance was about 520 cd/m<sup>2</sup>, and the luminous efficiency was 9.7 cd/A. When a continuous lighting test with constant current was carried out on these EL devices under the condition of the initial luminance of 300cd/m<sup>2</sup>, the half value period of luminance was about 700 hours.

Example 20

[0134] In Example 20, first, an ITO film was formed on a glass substrate. Next, on the ITO film, a two-layered organic light emitting layer was formed. First, N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine was deposited to form a first organic light emitting layer (thickness: 70nm). Furthermore, by codepositing 90wt% of N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine and 10wt% of A-1, a second organic light emitting layer (thickness: 30nm) containing electron injecting compound was formed on the first organic light emitting layer. Finally, a cathode (thickness: 100nm) made of Al was formed. When a DC voltage was applied to the thus produced EL device, stable luminescence was obtained. When the DC voltage was 10V, the luminance was about 450 cd/m<sup>2</sup>, and the luminous efficiency was 1.1 cd/A. When a continuous lighting test with constant current was carried out on these EL devices under the condition of initial luminance of 300cd/m<sup>2</sup>, the half value period of luminance was about 150 hours.

Example 21

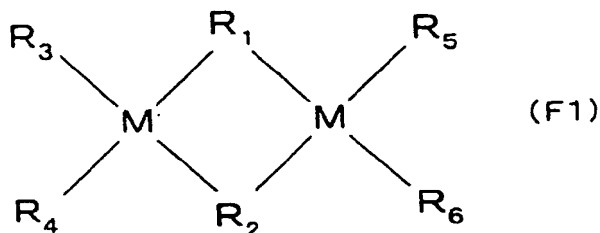
[0135] In Example 21, first, an ITO film was formed on a glass substrate. Next, on the ITO film, a hole transport layer (thickness: 50nm) made of N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine was formed. Next, a two-layered organic light emitting layer was formed. First, a first organic light emitting layer (thickness: 25nm) was formed by depositing Alq. Next, by codepositing 90wt% of Alq and 10wt% of A-1, a second organic light emitting layer (thickness: 25nm) containing electron injecting compound was formed. Herein, the first organic light emitting layer and the second organic light emitting layer were continuously formed. Finally, a cathode (thickness: 100nm) made of Al was formed. When a DC voltage was applied to the thus produced EL device, stable luminescence was obtained. When the DC voltage was 5V, the luminance was about 450 cd/m<sup>2</sup>, and the luminous efficiency was 4.3 cd/A. When a continuous lighting test with constant current was carried out on these EL devices under the condition of initial luminance of 300cd/m<sup>2</sup>, the half value period of luminance was about 500 hours.

explained. However, any one of those layers may be formed of an inorganic compound.

[0143] The above-mentioned compounds are available from Aldrich, ACROS ORGANICS, Tokyo Kasei Kogyo Co., Ltd. and LAMBDA PHYSIK.

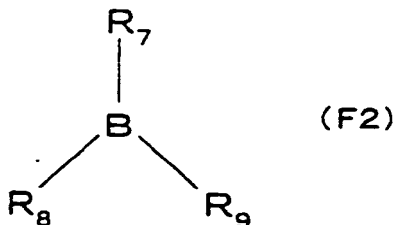
## Claims

1. An organic material for an electroluminescent device, which is a complex compound expressed by the formula (F1):



wherein  $R_1$  and  $R_2$ , which can be same or different, respectively denote one selected from the group consisting of halogen, alkyl having 1 to 3 carbon atoms, and a bridging ligand having a nitrogen-containing aromatic ring containing at least two nitrogen atoms, and when  $R_1$  or  $R_2$  is a bridging ligand having a nitrogen-containing aromatic ring, nitrogen in the nitrogen-containing aromatic ring is a coordinating atom;  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$ , which can be same or different, respectively denote one member selected from the group consisting of hydrogen, alkyl, aryl, an aryl derivative, a nitrogen-containing aromatic ring and a derivative of a nitrogen-containing aromatic ring; and M is a central metal.

2. The organic material for an electroluminescent device according to claim 1, wherein said complex compound has a pyrazabole structure.
3. The organic material for an electroluminescent device according to claim 2, wherein said complex compound is 4, 4', 8, 8'-tetrakis (1H-pyrazol-1-yl)pyrazabole.
4. An organic material for an electroluminescent device, which is an organic boron complex compound having an electron accepting phenyl group as a ligand.
5. The organic material for an electroluminescent device according to claim 4, wherein said boron organic complex compound is expressed by the formula (F2):



wherein  $R_7$  to  $R_9$ , which can be same or different, respectively denote an electron accepting phenyl group.

6. An electroluminescent device (10) comprising: an anode (12); a cathode (14); and an organic compound layer placed between said anode (12) and said cathode (14), wherein said organic compound layer (13) comprises the organic material as claimed in claim 1.
7. The electroluminescent device according to claim 6, wherein said organic material has a pyrazabole structure.
8. The electroluminescent device according to claim 6, wherein said organic material is 4, 4', 8, 8'-tetrakis (1H-pyrazol-1-yl)pyrazabole.

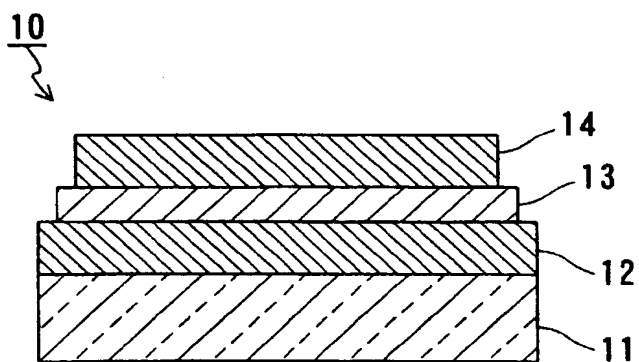


Fig. 1

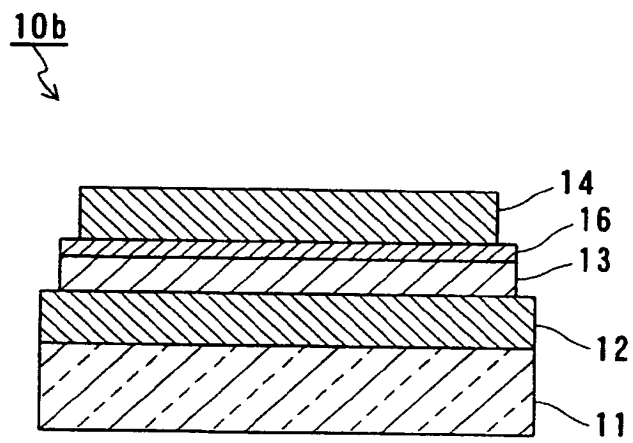


Fig.3

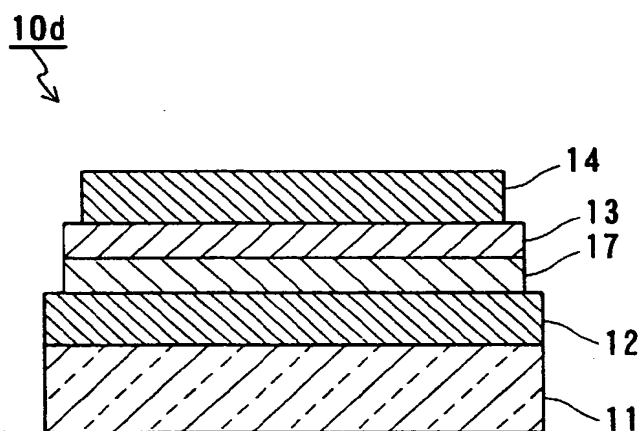


Fig.5

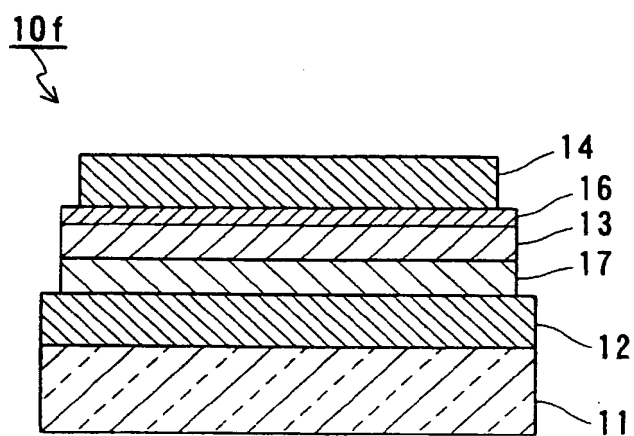


Fig. 7

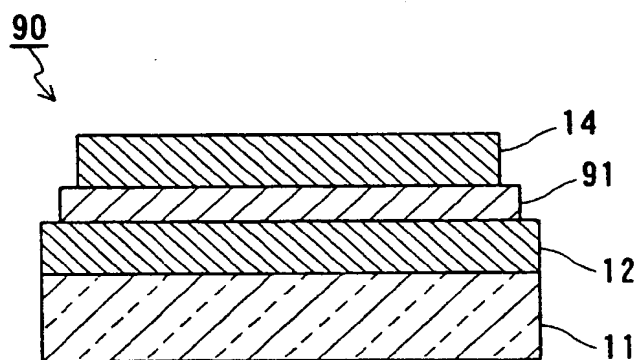


Fig.9

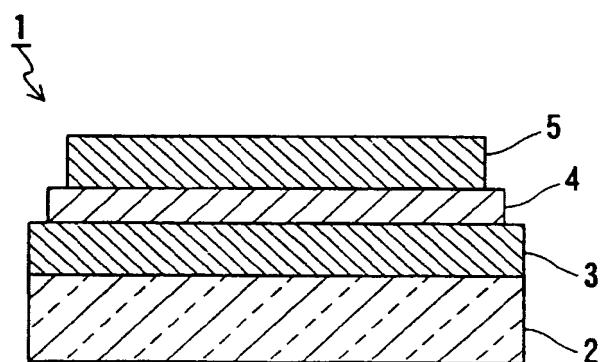


Fig.11  
PRIOR ART



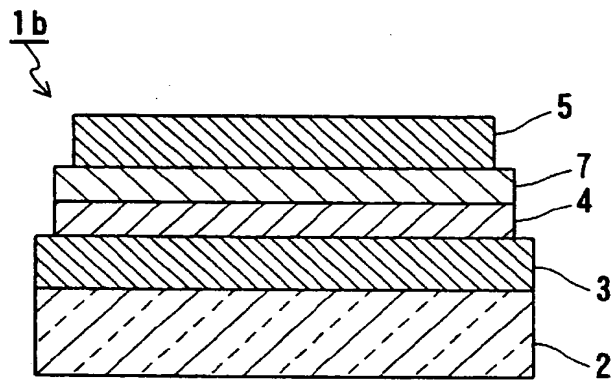
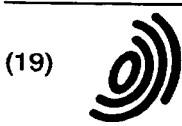


Fig.13  
PRIOR ART



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 026 222 A3

(12)

## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
06.09.2000 Bulletin 2000/36

(51) Int. Cl.<sup>7</sup>: C09K 11/06, H05B 33/14,  
C07F 5/05

(43) Date of publication A2:  
09.08.2000 Bulletin 2000/32

(21) Application number: 00102058.5

(22) Date of filing: 02.02.2000

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 04.02.1999 JP 2746899  
22.06.1999 JP 17498799  
29.07.1999 JP 21471299

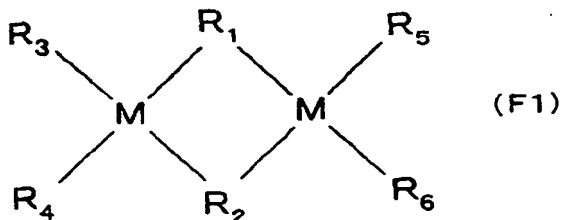
(71) Applicant:  
Matsushita Electric Industrial Co., Ltd.  
Kadoma-shi, Osaka-fu, 571-8501 (JP)

(72) Inventors:  
• Matsuo, Mikiko  
Nara-shi, Nara 631-0013 (JP)  
• Kishimoto, Yoshio  
Hirakata-shi, Osaka 573-0083 (JP)  
• Satou, Tetsuya  
Kadoma-shi, Osaka 573-0030 (JP)  
• Hisada, Hitoshi  
Toyonaka-shi, Osaka 565-0085 (JP)  
• Sugiura, Hisanori  
Hirakata-shi, Osaka 573-0049 (JP)

(74) Representative:  
Blumbach, Kramer & Partner GbR  
Radeckestrasse 43  
81245 München (DE)

(54) Organic material for electroluminescent device and electroluminescent device using the same

(57) A new organic material for an electroluminescent device suitable for an electroluminescent device and an electroluminescent device using the same. The organic material uses a complex compound expressed by the following formula (F1):



wherein R1 and R2, which can be same or different, respectively denote one selected from the group consisting of halogen, alkyl having 1 to 3 carbon atoms, and a bridging ligand having a nitrogen-containing aromatic ring containing at least two nitrogen atoms, and when R1 or R2 is a bridging ligand having a nitrogen-containing aromatic ring, nitrogen in the nitrogen-containing aromatic ring is a coordinating atom; R3, R4, R5 and R6, which can be same or different, respectively denote one member selected from the group consisting of hydrogen, alkyl, aryl, an aryl derivative, a nitrogen-containing aromatic ring and a derivative of a nitrogen-containing aromatic ring; and M is a central metal.

EP 1 026 222 A3



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 00 10 2058

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 3 681 381 A (TROFIMENKO SWIATOSLAW) 1 August 1972 (1972-08-01) * examples 3-5 *	1-3	C09K11/06 H05B33/14 C07F5/05
X	LEFFLER, JOHN E. ET AL: "Triarylboron anion radicals and the reductive cleavage of boron compounds" J. AMER. CHEM. SOC. (1970), 92(23), 6825-30, XP002139918 * page 6829, column 2, paragraph 4 *	4,5	
A	US 5 683 823 A (SHI JIANMIN ET AL) 4 November 1997 (1997-11-04) * column 7 - column 11; example 3 *	1-3,6-26	
A	WO 98 36035 A (UNIV KINGSTON) 20 August 1998 (1998-08-20) * page 2, line 28 * * page 4, line 14 - line 30 *	1-3,6-26	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C09K H05B C07F
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>9 June 2000</b>	Examiner <b>Shade, M</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

1



European Patent  
Office

Application Number

EP 00 10 2058

#### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

#### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☒ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims: